

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

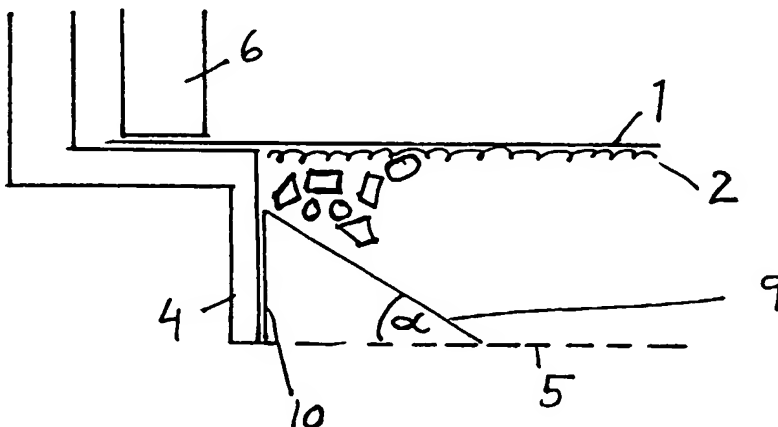
(19) World Intellectual Property
Organization
International Bureau(43) International Publication Date
15 January 2004 (15.01.2004)

PCT

(10) International Publication Number
WO 2004/005187 A1

- (51) International Patent Classification⁷: C01B 21/28 (74) Agent: ANDERSON, Elin; Norsk Hydro ASA, N-0240 Oslo (NO).
- (21) International Application Number: PCT/NO2002/000332 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 20 September 2002 (20.09.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 20023235 3 July 2002 (03.07.2002) NO (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): NORSK HYDRO ASA [NO/NO]; N-0240 Oslo (NO).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): ØIEN, Halvor [NO/NO]; Hvalenvegen 58, N-3943 Porsgrunn (NO). GRØNSTAD, Leif [NO/NO]; Gjerde, N-3766 Sannidal (NO). NIRISEN, Øystein [NO/NO]; Ytre Heistadv. 18B, N-3950 Brevik (NO). KARLSEN, Per, Ivar [NO/NO]; Markaveien 323, N-3947 Langangen (NO). SLÅEN, Magne [NO/NO]; Lakåsene 23, N-3739 Skien (NO).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: METHOD AND DEVICE FOR SUPPORTING CATALYST GAUZES IN AN AMMONIA OXIDATION BURNER



(57) Abstract: The invention comprise a support system for catalyst gauzes in an ammonia oxidation burner and a method of reducing movement of particulate ceramic material due to thermal dilatation. The catalyst gauzes (1) and possibly support screens (2) are being supported by ceramic fillings contained in a burner basket with metal walls and a perforated bottom plate. A "wave breaker" (9, 11) is fixed to the metal wall (4) and/or the outer part/periphery of the bottom plate (5).

Method and device for supporting catalyst gauzes in
an ammonia oxidation burner.

In a conventional ammonia oxidation burner a mixture of NH_3 , O_2 and N_2 react at elevated temperature and pressure over a platinum metal catalyst to nitrogen oxides.

5 Volatilised platinum is collected by a catchment material. Typically, both the catalyst and catchment material comprise a woven or knitted gauze and accordingly several such gauzes made into a pack secured to the burner structure by clamping means. The catalyst/catchment pack is placed on a support in the burner. The most commonly used type of support is ceramic rings, Raschig rings, placed in a basket secured to the burner
10 structure. Usually a support gauze of woven or knitted non precious metal, for instance "Megapyr", is placed between the main support and the catalyst/catchment pack. Such conventional burners are further described in Ullmanns Encyclopaedia, Vol. 20, pages 314-317, 4th Ed. If a N_2O decomposition catalyst is used in the burner, this will replace all or a part of the support material.

15

The ceramic rings and possible ceramic catalyst material often move away from the periphery during operation due to thermal dilatation. This movement creates a trough which often causes the gauze pack to tear. Especially around the outer edge of the gauzes the damage might be severe due to the lowered level of the Raschig rings there.

20 It is a common observation that the trough deepens with the number of starts and stops in the plant. This tearing represents a problem both due to loss of combustion efficiency, reduced cycle time and also a hazard problem. The ammonia slipping may form ammonium nitrate and ammonium nitrite in the downstream equipment, especially in the acid condenser. Ammonium nitrate and nitrite may decompose violently.

The object of the invention is to arrive at a support structure that would not cause damage to the catalyst pack during operation of the burner. Another object is to arrive at a system that prevents or reduces movement of particulate ceramic material during operation.

- 5 These and other objects of the invention are obtained with the method and support system as described below. The invention is further characterised by the patent claims. The invention will be described with reference to the drawings, Figure 1- 2 where

Figure 1 shows the formation of a trough in the ceramic fillings contained in a burner basket.

- 10 Figure 2 shows different configurations of the "wave breaker".

The invention thus concerns a method and a support system for reducing movement of particulate ceramic material and avoiding tearing of catalyst gauzes in an ammonia oxidation burner. The catalyst gauzes and possibly support screens are being supported by ceramic fillings and possible catalyst material contained in a burner basket with
15 metal walls and perforated bottom plate. A "wave breaker" is preferably fixed to the metal wall of the burner basket or alternatively to the periphery of the bottom plate of the burner basket. The ceramic fillings will then move along with the metal wall during expansion. It is preferred that the "wave breaker" is perforated and filled with ceramic fillings or similar material to obtain the same flow resistance as the filling material of
20 the bed. The "wave breaker" could be in the form of a triangular shaped ridge. It could be a right-angled triangle with the right angled wall fixed to the metal wall, or an equilateral triangle fixed to the periphery of the bottom plate. The "wave breaker" could also be a smooth or perforated sheet arranged at an angle of 10-60° to the wall. A preferred angle is 25-35°. The ridge or sheet could be made of segments and the
25 segments could have an end wall. It is also possible to use a "wave breaker" in the form of a honeycomb structure, preferably with a sloping top.

Initial tests in small scale indicated that an important factor for the formation of the trough is the difference in expansion of the Raschig rings and metal support due to temperature variation. After only a few cycles of expansion without any support systems in the bed a trough was created, and part of the outer edge became empty of rings. This is similar to observations from burners which have been in operation. The cause of the trough formation is believed to be the difference in thermal expansion in the metal of the burner basket and the ceramic Raschig rings. In the larger plants with up to 5 m in burner diameter, the thermal expansion of the metal basket are up to 30 mm on the radius, caused by heating from ambient to operation temperature.

- 10 In figure 1 the effect of the heat variations is illustrated. Figure 1A shows schematically the equipment before start. The ammonia oxidation burner comprises a catalyst layer, usually in the form of a plurality of woven or knitted gauzes of Pt/Rh wire and normally a catchment layer of getter material, for instance a palladium alloy in the form of woven or knitted gauzes. All these gauzes form a pack 1 resting on a steel screen 2 supported
15 by a layer of Raschig rings 3 placed in a basket with metal wall 4 and perforated bottom plate 5. Some or all of the Raschig rings may be replaced by a ceramic catalyst. The catalyst pack, the catchment pack and the support gauze are secured to the circumference of the burner on a ledge by fixing weights 6 or similar arrangement. The basket is also secured to the burner wall at about the same place. Before start the Raschig rings
20 bed is levelled, and the steel screen and the catalyst gauze pack are installed and fixed around the periphery.

After the first start, the metal wall and perforated bottom plate expands more than the Raschig rings. This means that the Raschig rings will not expand and fill the gap after the metal wall has moved outwards. This situation is illustrated in Figure 1B.

When the plant shuts down the metal wall cools and contracts, and the Raschig rings at the periphery are pushed inwards with respect to their original position. Figure 1C shows a vertical section view of a conventional catalyst and catchment gauze pack and its support at the end of a campaign. Here a trough is formed which often causes the
5 gauzes to tear. This tearing represents a problem both due to loss of combustion efficiency, reduced campaign length and also a hazard problem.

It is the rings close to the periphery that moves. To overcome this problem it was suggested to install a support structure, also called "wave breaker", in the bed to prevent the creation of a trough. Based on the initial experiments a test unit was constructed
10 with dimensions as one part from centre to periphery of an average burner. To simulate temperature expansion, hydraulic force was installed to be able to move one of the short walls. The pilot test will not be able to reproduce the expansion over the whole radius of the burner, but can reproduce the net effect at one end of the compartment. The number of expansions of a burner in operation are dependent on the number of shut downs
15 during one campaign, this number varies between 1 and 10.

The first step was to recreate the phenomenon with the trough which is formed at the periphery of the Raschig ring bed during operation. This point was of importance to see whether the temperature expansion could be regarded as one of the main reasons. This was done to simulate the temperature expansion by only moving the movable wall with
20 different expansion lengths. The different expansion lengths used were 70, 50 and 30 mm. To simulate the variation in temperature during normal operation expansion, first an outward stroke with 30 mm (start-up) and then consecutive inward and outward strokes of 10 mm were used. After only a few cycles of movement the trough was created, and part of the outer edge was empty of rings. This is similar to observations
25 done in burners which have been in operation. Even with only 10 mm repetitive expansion/ contractions the pilot test unit was able to recreate the formation of the trough.

Different "wave breakers" were tried out in the pilot plant and these are illustrated in figure 2 . The tested shapes were a short and long honeycomb structure, a smooth or perforated sheet at different angles and a triangular shaped ridge.

First the short "honeycomb" as shown in Figure 2D was placed in the bed next to the
5 movable wall without being fastened, and the rings were filled in. The result of an expansion of 30 mm was that the support system started to move inwards and upwards in the bed, at the same time as the trough was created. After 8 cycles the entire support system had risen above the Raschig ring bed, and part of the outer edge was empty of rings. A perforated bottom was welded on to the "honeycomb" support system, and
10 placed in the bed as in the previous experiment. The support system moved somewhat up in the bed, but was stabilised and did not move to the top of the bed. There was however no improvement of the formation of the trough.

A "honeycomb" support system with bottom was then welded to the movable wall. The results of the expansion then was that the trough was created outside of the
15 "honeycomb", but the rings in the chambers did not move at all. The trough was smaller than in the previous experiments, but after 6 cycles the outer edge of the support system became visible in the bed.

Experiments with the long honeycomb structure (Fig. 2C) were also carried out. It was found that the best results were obtained when the support structure was welded to the
20 movable wall and part of the support structure was cut off as shown in Figure 2E.

The short and long honeycomb support system penetrated the top of the Raschig ring layer in most cases. This can result in sharp edges cutting the gauze, even without the trough formation. When the top of the honeycomb support was cut with a sloping top 8, the performance improved and the support did not penetrate the top of the Raschig rings
25 bed. This system with many small compartments will probably be somewhat more

complicated to handle, since all compartments must be filled with rings. If there is mounted a perforated bottom in the compartments, they can however be lifted out as complete sections.

Experiments were also carried out with a smooth sheet 9 placed in the bed at two different angles α 60 and 75 ° as illustrated in Figure 2A. The sheet was welded to the movable wall and three support wedges 10 were welded to the sheet. The smooth sheet installed with an angle of 60° gave the best results with no permanent trough formation. Alternatively it could be a right-angled triangle with the right angled wall fixed to the metal wall. The solution with a sloping sheet is dependent on the roughness of the sheet and the sloping angle. If the angle is reduced, more of the area in the burner is covered. When the sheet is not perforated, the flow area in the burner will be reduced and creating higher pressure drop and uneven flow over the catalyst gauze.

A perforated sheet (5mm holes) was placed in the bed with different angles, 60°, 45° and 30°. The sheet was welded to the movable wall and three support wedges were welded to the sheet. The results are given in Table 1:

Table 1.

α	Expansion length, mm	Number of cycles	Depth of trough, mm	Length*, mm
60	30	1	15	
60	30	2	35	250
60	30	5	50	350
60	30	2.5	30	3 50 ¹
60	30	3	30	250
60	30	5	40	400
60	30	2.5	40	3 50 ²
60	30	5	50	350
45	30	0.5	10	200
45	30	2.5	20	3 00 ³
45	30	5	25	300
45	30	5.5	30	350
45	30	10	30	350
45	30	14.5	35	400

45	30	15	35	400
45	30	24.5	40	400
45	30	34.5	40	400
45	30	35	35	350
30	30	0.5	0	
30	30	1	0	
30	30	1.5	20	4
30	30	2	0	
30	30	2.5	30	
30	30	5	0	
30	30	5.5	30	
30	30	10	20	5
30	30	10.5	35	
30	30	15	25	
30	30	15.5	35	
30	30	20	20	

*length from the movable wall to the trough (if the trough is created away from the movable wall).

1. h=250
- 5 2. h= 300
3. The trough is created next to the movable wall
4. The trough has moved into the bed, about 300 mm.
5. The trough is permanent

With an angle of 60° a trough was created next to the movable wall (50 mm at 5 cycles).

- 10 Also with 45° a trough was created at the wall, but the size was reduced compared to 60° (35 mm at 35 cycles). By using a sheet with 30° slope the trough moved about 300 mm into the bed and the depth was also reduced (20 mm at 20 cycles).

- Experiments were also carried out with a triangular shaped ridge 11 (pyramid shaped support) of perforated sheets (5 mm). It was first placed in the bed without being
- 15 welded to the movable wall. With this arrangement hardly any improvement in the through formation was observed. If this support is not fastened there is a possibility that the top of the pyramid will penetrate the bed and result in sharp edges that can tear the

gauze. When the support was welded to the wall, the support followed the movements and a trough was formed outside the top of the support. This trough was significantly shallower than what was observed without the wave breaker installed. The installation of the triangular shaped ridge that moves with the outer wall or the outer part of the perforated bottom, will move the Raschig rings together with the metal. When the trough is created closer to the centre of the burner basket, the height difference will be smaller.

In the following the results are given for the experiments with a pyramid shaped "wave breaker". A triangular ridge (pyramid shaped) was arranged along the outer wall. The height of the ridge was 100 mm and the angle between the floor and the side was 45°. The edge of the ridge was at the closest approximately 50 mm from the outer wall. The ridge was fixed to the outer wall. The height of Raschig rings was 130 mm -300 mm.

Table 2. Results of wall movements with pyramid shaped "wave breaker".

Test No.	Height of rings (mm)	Wall movement (mm)	Depth of trough (mm)	Width of trough (mm)
1	130	30	35	300
2	130	30	25	300
3	130	30	35	300
4	130	30/10	20	300
5	130	30/10	30	300
6	130	30/10	25	300
7	200	35	20	250
8	200	30/10	25	300
9	300	30/10	25	350

The trough that is formed is a rather flat depression with no sharp edges or steep falls.

With regard to the trough formation and operation of the burners the solution with the perforated sloping sheets seems to be the best. With an angle of 30° to the horizontal plane the trough was formed away from the wall and the depth was significantly reduced compared to the original. When the trough is formed somewhat away from the wall the

tearing forces on the gauze will be reduced. We avoid the concentration of forces due to the gauze weight and the trough formation too close together.

Almost all the wave breakers that were tried gave better results than the use of no support at all. It would also be possible to use for example a sinusoidally shaped metal
5 band fixed to the metal wall. This could be placed just below the steel screen.

In burners which are in operation, expansion occurs over the whole radius. In pilot test unit the expansion is concentrated at a relatively short distance close to the movable wall, but the test unit recreate the trough as it is seen in operation. Both "wave breakers" in the form of a triangular shaped ridge and a sloping sheet have been tested out in full
10 scale in the factory and the results from the pilot test is confirmed. When a smooth sheet is used, the angle is not of importance as the Rashig rings slide easily on this material. However, when perforated sheets are used the correct angle is important.

Patent claims

1. A support system for catalyst gauzes in an ammonia oxidation burner, where the catalyst gauzes (1) and possibly support screens are being supported by ceramic fillings (3) and/ or catalyst contained in a burner basket with metal walls (4) and a
5 perforated bottom plate (5),
characterized in that a "wave breaker" (9,11) is fixed to the metal wall and/or the outer part /periphery of the bottom plate.
2. A support system according to claim 1,
characterized in that the "wave breaker" is filled with ceramic fillings/
10 catalyst or similar material to obtain the same flow resistance as the filling material of the bed.
3. A support system according to claim 1,
characterized in that the "wave breaker" is a triangular shaped ridge
(11).
- 15 4. A support system according to claim 1,
characterized in that the "wave breaker" is a smooth or perforated sheet (9) arranged at an angle of 10-60 ° to the wall.
5. A support system according to claim 4,
characterized in that the angle is 25-35°.
- 20 6. A support system according to claim 3, 4 or 5,
characterized in that wave breaker is made of segments.

7. A support system according to claim 6,
c h a r a c t e r i z e d i n t h a t the segments have end walls.
8. A support system according to claim 1,
c h a r a c t e r i z e d i n t h a t the "wave breaker" is a honeycomb structure.
- 5 9. A support system according to claim 8,
c h a r a c t e r i z e d i n t h a t the honeycomb structure has a sloping top (8).
10. A method of reducing movement of ceramic material and avoiding tearing of
catalyst gauzes in an ammonia oxidation burner where the catalyst gauzes and
possibly support screens are being supported by ceramic fillings and possibly a
10 catalyst on a perforated plate or contained in a burner basket with metal walls and
perforated bottom plate,
c h a r a c t e r i z e d i n t h a t a "wave breaker" is fixed to the metal wall and/or
the outer part/periphery of the bottom plate of the burner basket and moves the
ceramic material together with the metal wall during expansion.
- 15 11. Method according to claim 9,
c h a r a c t e r i z e d i n t h a t it is used a "wave breaker" formed like a triangu-
lar shaped ridge, a smooth or perforated sheet or a honeycomb structure.

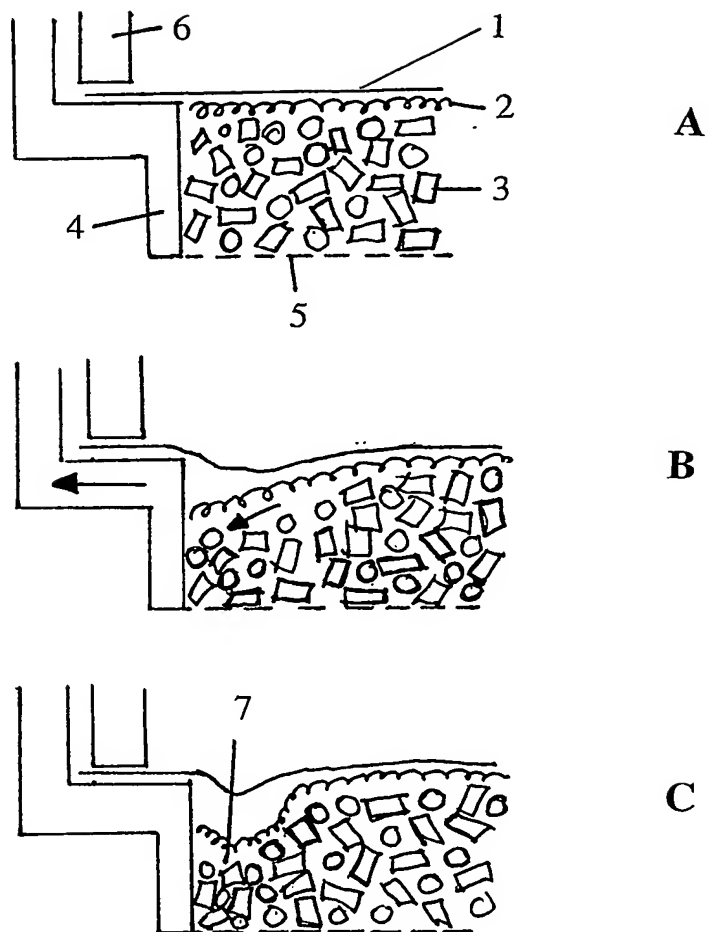


FIG. 1

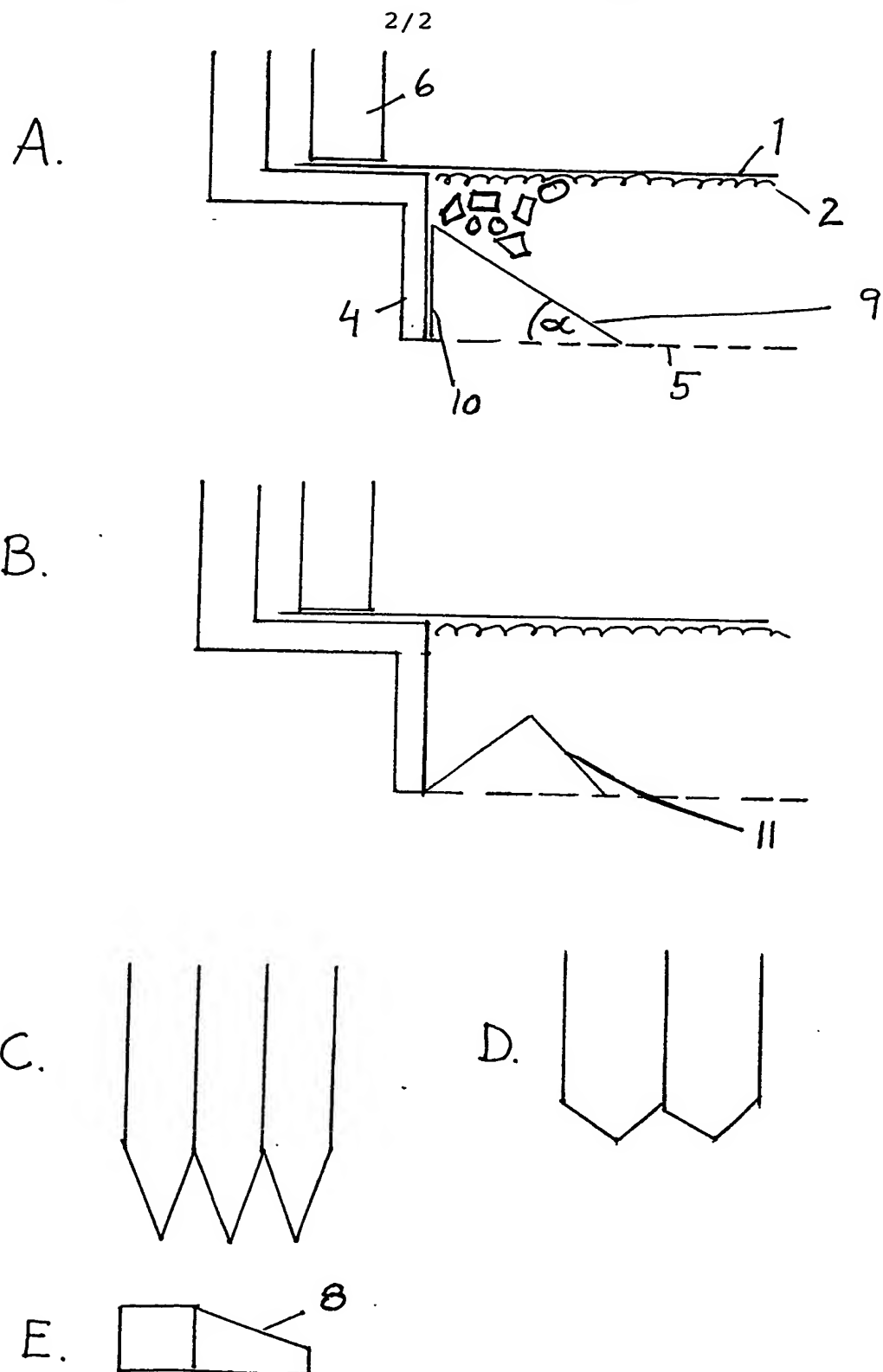


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 02/00332

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C01B 21/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C01B, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9108982 A1 (NORSK HYDRO A.S.), 27 June 1991 (27.06.91) --	1-11
A	GB 2274071 A (PGP INDUSTRIES INC), 13 July 1994 (13.07.94) --	1-11
A	WO 8603479 A1 (JOHNSON MATTHEY PUBLIC LIMITED COMPANY), 19 June 1986 (19.06.86) --	1-11
A	DE 2754643 A1 (DAVY POWERGAS GMBH), 13 June 1979 (13.06.79) -- -----	1-11

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

14 April 2003

Date of mailing of the international search report

5 -04- 2003

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Bertil Dahl/ELY

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

29/03/03

International application No.

PC 02/00332

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
WO	9108982	A1	27/06/91	AU 6717090 A NO 168689 B,C NO 895017 A	18/07/91 16/12/91 14/06/91
GB	2274071	A	13/07/94	AU 5820194 A GB 2278462 A,B GB 9300157 D GB 9415049 D WO 9415711 A	15/08/94 30/11/94 00/00/00 00/00/00 21/07/94
WO	8603479	A1	19/06/86	GB 2141042 A,B GB 8406363 D BR 8407375 A EP 0204696 A GB 2152637 A,B GB 8400428 D JP 62501411 T	12/12/84 00/00/00 10/03/87 17/12/86 07/08/85 00/00/00 11/06/87
DE	2754643	A1	13/06/79	NONE	